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Determination of Electron Affinity
Differences by Surface Ionization*

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INTRODUCTION

Determination of electron affinities by surface ionization has long been a field of great interest. Several factors make experimental negative ion current measurements difficult. Relatively high temperatures are required for negative ion emission, hence, thermionic electrons are also emitted and contribute to the negative ion current. The electrons may also form negative ions in gas phase collisions and thereby tend to obscure the effects of the surface ionization. Various methods, such as keeping the surface temperature low so the electron emission is small¹ and suppressing the electrons with a magnetic field parallel to the cathode,² have been used to separate the effect of thermoelectrons from ion emission. The former method allows excessive contamination of the surface by gas atoms leading to erroneous results. Both methods require the assumption that the negative ion current is due to a single species. Mass spectrometric methods prove far superior to either of the above techniques since not only are the electron and ion beams separated but identification of the emitted ions is made possible.

Several papers involving determinations of electron affinity differences^{3,4} of the halogens utilizing mass analysis of the product ions have been published. These experiments were largely limited to filaments surrounded by dilute atmospheres of diatomic interhalogen compounds or double beams of alkali halides directed upon a hot filament. In this work a well collimated molecular beam is incident upon a small portion of a tungsten ribbon filament so that there should be a negligible temperature gradient across the beam-surface interface. The purpose of these experiments is to explore the feasibility of using polyatomic molecules containing two electronegative species for the determination of electron affinity differences, and to examine the extent of dissociation of such molecules on a hot tungsten surface as a function of surface temperature.

THEORY

The electron affinity, $E(X)$, of an atom X is defined as the energy at 0°K of the electron attachment reaction.



This quantity may be obtained from a measurement of the equilibrium constant, K_p , for the reaction. For (1),

$$\ln K_p = \ln(P_{X^-}/P_X P_e) = -\Delta F^{(0)}/RT \quad (2)$$

or,

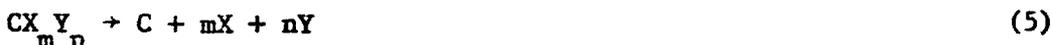
$$RT \ln K_p = -E(X) + F_e^{(0)} + F_X^{(0)} - F_{X^-}^{(0)} \quad (3)$$

where $F_i^{(0)}$ are the free energies of the reactants and products chosen so that they are zero at 0°K and P_i equal to one atmosphere. The partial pressures, P_i , may be calculated from the numbers, Z_i , of species i being emitted from a hot surface at temperature T from the relation

$$P_i = Z_i (2\pi m_i kT)^{1/2} \quad (4)$$

The method of electron affinity differences used in this work involves the measurement of negative ion currents of X^- and Y^- emitted from a hot tungsten surface upon which impinges a beam of molecules of the type $CX_m Y_n$, where $X=F$ and $Y=Cl$. The ratio of these currents then gives the difference in the electron affinities of the two halogens.

If a $CX_m Y_n$ molecule dissociates on a hot surface according to



equilibrium between the two halogens emitted from the surface will exist as



For (6),

$$-\Delta F^{(o)}/RT = \ln K_p = \ln[(Z_{X^-}/Z_{Y^-})(Z_Y/Z_X)] \quad (7)$$

and,

$$-\Delta F^{(o)} = E(X) - E(Y) + (F_X^{(o)} - F_{X^-}^{(o)}) - (F_Y^{(o)} - F_{Y^-}^{(o)}) \quad (8)$$

The $F_i^{(o)}$ may be evaluated in terms of Q_i , the internal partition functions of species i . Substituting this with (8) into (7) gives the difference between the electron affinities of X and Y :

$$E(X) - E(Y) = RT \ln[(Z_{X^-}/Z_{Y^-})(Z_Y/Z_X)(Q_{Y^-}/Q_{X^-})(Q_X/Q_Y)] \quad (9)$$

Z_{X^-}/Z_{Y^-} is simply the ratio of the emitted ion currents. Z_Y/Z_X is the ratio of the numbers of Y and X atoms leaving the surface or the ratio of their concentrations on the surface and is equal to n/m since $Z_{X^-} \ll Z_X$ and $Z_{Y^-} \ll Z_Y$. Hence

$$\ln[(I_{X^-}/I_{Y^-})(Q_{Y^-}/Q_{X^-})(Q_X/Q_Y)] = \{[E(X) - E(Y)]/RT\} \ln m/n \quad (10)$$

Therefore the slope of a plot of the left hand side of (10) vs $1/T$ gives the electron affinity difference and the intercept at $1/T=0$ gives m/n , if the dissociation on the surface is complete.

The electronic partition function of the X and Y atoms is given by

$$Q = g_0 + \sum g_j \exp(-E_j/kT) \quad (11)$$

where g_0 and g_j are the degeneracies of the ground and j^{th} excited states respectively and E_j is the difference in the energies of the two states. Fluorine and chlorine each have a low-lying $^2P_{1/2}$ excited state of energies above the $^2P_{3/2}$ ground state corresponding to 404 and 881 cm^{-1} respectively. The ions in the ground states possess 1S_0 configurations and presumably have no low-lying excited states. Hence the ratio of fluorine to chlorine partition functions is

$$Q_F/Q_{Cl} = [4 + 2 \exp(-404 \times 1.439/T)] / [4 + 2 \exp(-881 \times 1.439/T)] \quad (12)$$

If the assumptions made above are correct the ratio of the ion currents is independent of the work function of the surface and the beam flux incident upon the surface. Also, it must be assumed that the accommodation coefficients for electron exchange between the surface and X and Y atoms on the surface are unity.

APPARATUS

The apparatus is shown schematically in Fig. 1. The gas is introduced into chamber 1 where it effuses out of a 1/2 mm orifice at (a) and is collimated by orifices (b) and (c). The beam then impinges upon a polycrystalline tungsten filament (f) and the ions are extracted and accelerated by a series of electrodes at (e) and (g). The ion beam enters a 3 inch radius-of-curvature 90° magnetic deflection mass spectrometer and strikes the cathode of a Bendix magnetic electron multiplier. The output currents of the multiplier are measured with a Keithley electrometer amplifier. The lower limit of measurement of ion currents is approximately 2×10^{-16} amp. Chambers 2, 3, and 4 and the analyzer tube of the mass spectrometer are all separately pumped resulting in background pressures of about 10^{-7} torr in the reaction chamber (#4). A beam shutter located in chamber 3 allows interruption of the molecular beam so that the background ion current due to both surface ionization and electron bombardment of the residual gas may be measured.

MEASUREMENTS

The pressure of the reactant gas is raised in the beam source (Chamber #1, Fig. 1) and a beam is formed which strikes the target filament. The ions are extracted from the filament and focused on the entrance slit of the mass spectrometer. The ion energy upon entrance to the mass spectrometer is 1000 volts. The mass spectrum is swept and peaks are observed at m/e of 16, 19, 35, and 37. Mass 16 (O^-) is assumed to arise from electron bombardment of background gas and oxides on the filament. Masses 19, 35, and 37 are F^- , $(Cl^{35})^-$, and $(Cl^{37})^-$. The $(Cl^{37})^-$ to $(Cl^{35})^-$ ratio is 1/3 in all cases. Peaks 19 and 35 were swept successively and their ratio, corrected for $(Cl^{37})^-$, taken as a function of the filament temperature. The temperature measurements were made by sighting on the filament with an optical pyrometer of the disappearing filament type.

RESULTS

Figure 2 shows a plot of $\log[(I_F^-/I_{Cl}^-)]$ vs $1/T$ for CF_3Cl , CHF_2Cl , CF_2Cl_2 , and $CFC1_3$. The straight lines are assigned a slope corresponding to $E(Cl) - E(F)$ equal to 0.20 eV as reported by Bailey³ and are fitted to the experimental points at high temperatures by the method of least squares. The plots indicate the correct trend of the intercepts to higher values of m/n as the F to Cl atom ratio increases in each molecule. However, the intercepts are far below the values expected if the molecules are completely dissociated on the surface. Table 1 gives the theoretical and observed values of m/n .

Table 1.

$\frac{CF}{m} \frac{Cl}{n}$	$(m/n)_{theory}$	$(m/n)_{obs.}$
CF_3Cl	3	0.56
CHF_2Cl	2	0.35
CF_2Cl_2	1	0.23
$CFC1_3$	1/3	0.12

Over a portion of the temperature range covered the straight line fits the experimental points fairly well. This combined with the low values of the intercepts suggests that the molecules are incompletely dissociated on the surface and that the degree of dissociation, although not unity, is at least constant over some temperature interval. The change in slope at lower temperatures indicates that the degree of dissociation is changing in this temperature range. It should be noted that the straight line portion of the plots extends over a greater range of temperatures and that the fall off is less steep as the F to Cl atom ratio decreases.

No peaks corresponding to undissociated fragments of the molecules (e.g. CF^-) were observed. If such ions are emitted from the surface then the electron affinities of the radicals must be ≤ 3 eV.

CONCLUSIONS

It is not evident why the degree of dissociation should be constant at the higher temperatures when it is still less than unity. The increasing degree of dissociation at lower temperatures may be explained by considering the C-F and the C-Cl bond strengths. The average C-F bond strength is about 4.4 eV and the average C-Cl bond strength is about 3.3 eV. As the temperature increases the relative probability of breaking a C-F bond to that of breaking a C-Cl bond increases.

These results indicate that polyatomic molecules can be used at sufficiently high temperatures for determining electron affinity differences, although the results are not completely satisfying because of the incomplete dissociation observed.

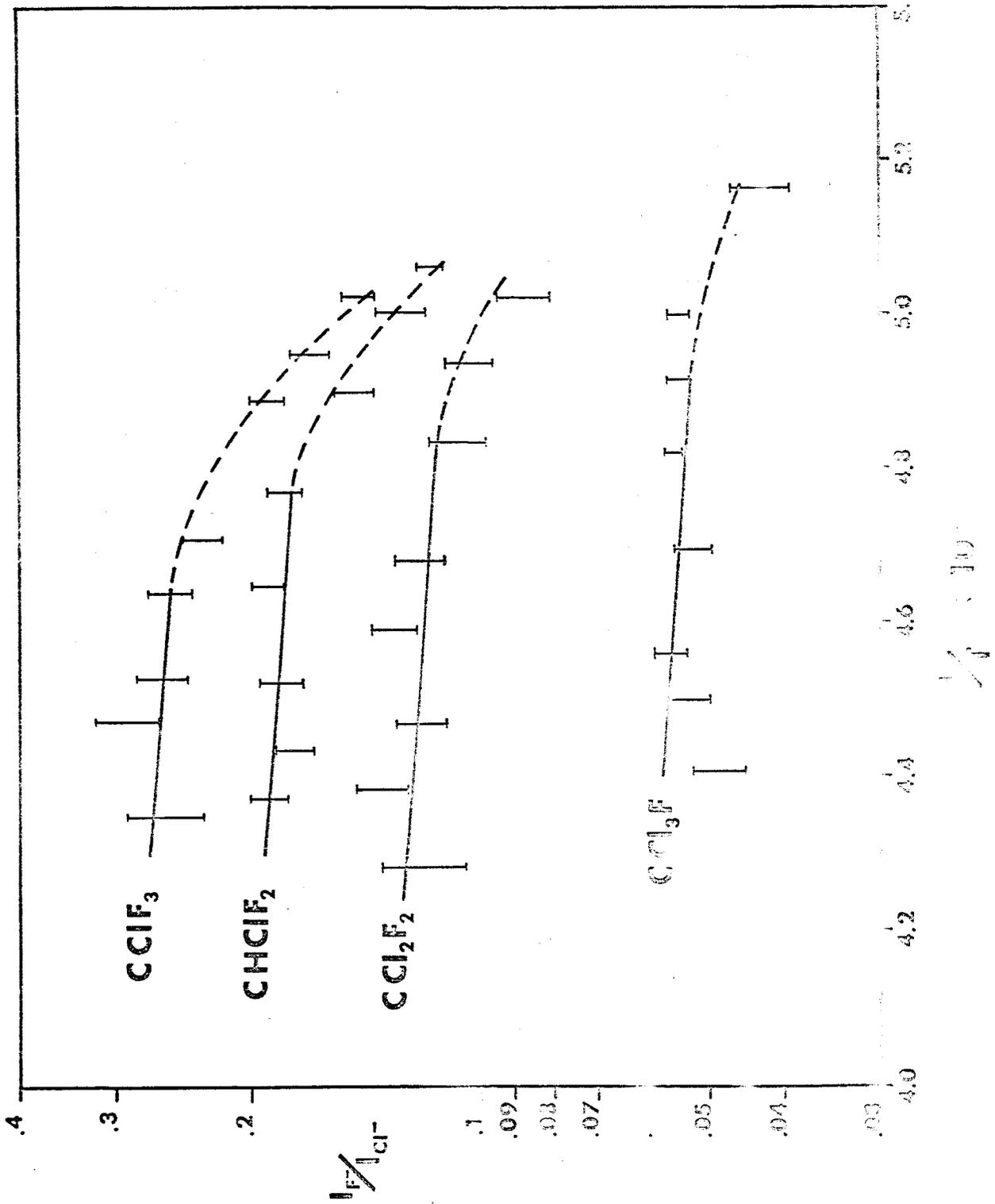
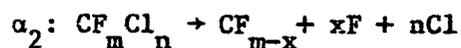
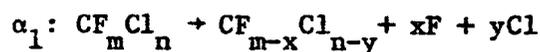


Fig. 2: I_X/I_Y vs $1/T$

A degree of dissociation for each molecule may be calculated from the value of the intercept of the plot in Fig. 2. If no assumptions are made as to the nature of the dissociation then $\alpha_1 = [(m/n)_{\text{obs}} / (m/n)_{\text{theory}}]$ gives the degree of dissociation in the temperature interval of its constancy. A reasonable assumption to make, however, is that the C-Cl bonds are completely broken. Then one can obtain a degree of dissociation of the C-F bonds, $\alpha_2 = x/(m-x)$. Table 2 gives the results of calculating these two degrees of dissociation.

Table 2.

CF_mCl_n	α_1	α_2
CF_3Cl	0.18	0.23
CHF_2Cl	0.18	0.21
CF_2Cl_2	0.23	0.30
CFCl_3	0.36	0.56



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